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FORMALDEHYDE WASTEWATER CLEANING IN WOODWORKING INDUSTRY

The paper represents the results of research the sorption, oxidation and condensation methods of neutralization of liquid waste formaldehyde woodworking companies. The paper presents data on the neutralization degree of liquid waste in terms of formaldehyde and chemical oxygen demand value.

Introduction. Urea- , phenol - and melamine-formaldehyde resins are widely used in the production of particleboard, plywood, furniture and other wood composite materials.

According to the technological wastewater standards wastewater in an amount of 26 m^3 per 1000 m^3 of production is generated during the production and use of resins and adhesive compositions in the washing process equipment plants, storage tanks, pipelines. The composition of washing wastewater is characterized by containing formaldehyde, phenol, methanol, soluble and insoluble products of condensation oligomer (phenol) and the other components [1 , 2] .

Along with the washing water the concentrated liquid wastes are formed in the process of the manufacture and application of resins. These wastes are neutralized by thermal methods or stored in a storage medium.

In the Republic of Belarus in the next two years it is planned to increase the production of wood composite materials. It should lead to a significant increase in the volume of washing wastewater. At present enterprises washing wastewater is treated virtually and discharged into the liquid waste storage or in the sewer after dilution.

Oxidative degradation (vapor phase and liquid-phase oxidation, electrochemical oxidation, biochemical oxidation, photochemical oxidation) and physical and chemical cleaning methods (sorption, flotation, coagulation, chemical treatment)find the greatest distribution to neutralize the same or similar composition of washing water. However, the use of these methods for cleaning washing wastewater is not very efficient or is associated with significant cost and secondary pollution of water.

Main part. The paper objective is to appreciate the effectiveness of various methods of treatment of liquid waste to develop a method for neutralizing them with subsequent biological refining.

The research objective was the liquid waste selected from the storage of LtD "Mostovdrev" (Mosty town). The storage is designed for 2,400 m^3 of waste. The composition of wastewater is characterized by the value of COD – 42,000 mg O_2/dm^3, formaldehyde concentrations (5 g/dm^3), free phenol (360 mg/dm^3), and methanol (5.4 g/dm^3). The storage is not currently used, and there is the problem of its disposal. When chosen a liquid waste processing conditions it was taken into account that the deactivation should be spent directly in the drive.

Some investigations of efficiency of liquid waste decontamination by methods of adsorption, oxidative degradation of dissolved compounds condensation to form the solid phase were carried out during the research work.

Activated carbon AG-3, outspent ion exchange resins, wood ash were used in studies as adsorbents.

When handling liquid waste with adsorbent AG-3 the maximum degree of purification (38% COD) is achieved at an adsorbent dose of 40 g/dm^3 (Fig. 1).

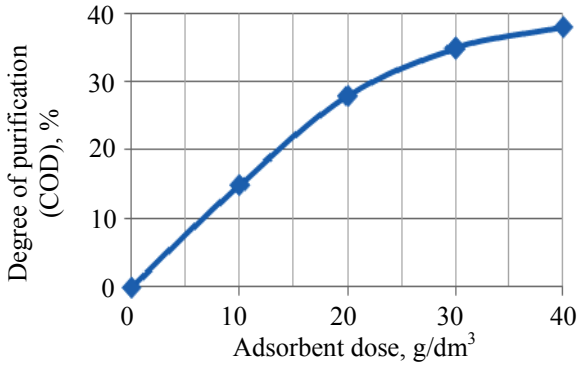

Fig. 1. The relationship between purification degree and adsorbentAG-3 dose

Under certain conditions synthetic ion exchange resins can absorb formaldehyde and phenols but ion exchangers are not used for wastewater cleaning from these pollutants because of their high cost and complexity of regeneration. The outspent ion exchange resins were used as absorbers in the researches.

Processing of samples of liquid waste spent with anion AN-31 can reduce COD of liquid waste by 12%. Formaldehyde content while is being decreased by 20% (Fig. 2).

The amount of COD decreases by 41%, and the concentration of formaldehyde decreases by 74.5%when40 $g/dm^3$of outspent ion exchange resinAV-17-8 were used as a sorbent (Fig.3). A higher degree of purification in comparison with the anion exchanger AN-31 can be explained by the interaction of formaldehyde with quaternary ammonium groups forming part of the ion exchanger.

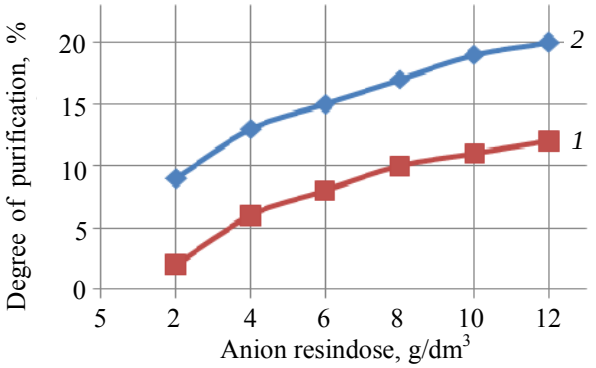

Fig. 2. The relationship between purification degree and anion resinAN-31dose:
1 – Formaldehyde; *2* – COD

The content of free phenol is reduced by more than 50% when liquid waste being processed by outspent ion exchanger AV-17-8. Sorption capacity for formaldehyde at the same doses of adsorbent for AN-31 is 0.1 g/g and for AV-17-8 is 0.2 g/g.

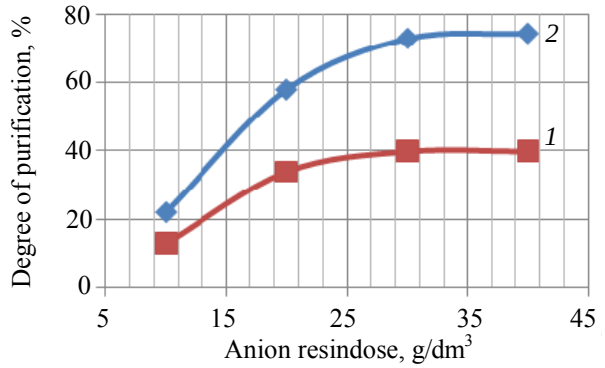

Fig. 3. The relationship between purification degree and outspent ion exchange resinAB-17-8dose:
1 – Formaldehyde; *2* – COD

The using of ion exchanger KU-2-8 and wood ash as a sorbent did not change the composition of the liquid waste.

While using adsorbents for liquid waste treatment the amount of COD, the concentration of formaldehyde and other substances cannot be reduced to a level enable into accomplish the polishing treatment by biological method.

Oxidation is a common method of neutralization of water waste and liquid wastes containing organic compounds. Air oxygen and hydrogen peroxide were used as oxidants in the process of studies on the oxidative deactivation of wastewater. Air oxidation was carried out by aeration of liquid waste samples. The samples were basified with sulfuric acid or calcium hydroxide suspension to investigate the influence of pH on the oxidation of organic substances. The aeration using reduces COD by 5% in acid and by 6% in the alkaline environment. The reducing of the content of polluting substances can be caused by oxidation as well as air stripping of volatile compounds.

The hydrogen peroxide treatment was performed under stirring and aged for 1 day at 20 °C. The consumption of hydrogen peroxide was 3.0–13.8 g/dm^3. The amount of COD of waterwaste after such treatment (loss of hydrogen peroxide is 13 g/dm^3) was decreased by 9%.It indicates the low processing efficiency in these conditions.

The effective method for the oxidation of organic pollutants is their treatment by mixture of hydrogen peroxide and ferric iron (Fenton's reagent). The Fenton reaction is based on decomposition of hydrogen peroxide catalyzed by iron (II) to give hydroxyl radicals [3].Fenton's reagent oxidation efficiency depends on the concentration of H_2O_2 and Fe^{2+}, pH and treatment time. The treatment by composition of hydrogen peroxide and iron salts provides a significant decrease of pollutants in the liquid wastes. The maximum effect of neutralization on COD (41%) is achieved when the amount of hydrogen peroxide is no less than 13 g/dm^3. At the same time it is somewhat higher than if it only treated with hydrogen peroxide at comparable concentrations of oxidant.

The phenol from the concentrated waste water can be recovered as products of condensation with formaldehyde which are formed in the presence of acids with an excess amount of formaldehyde. The liquid wastes were acidified to pH 2, stirred, and kept a certain time to initiate the condensation reaction. COD value of wastewater after its holding for 14 days was reduced by 69% (Fig. 4). It is associated with condensation and transition of phenolic alcohols into the sediment.

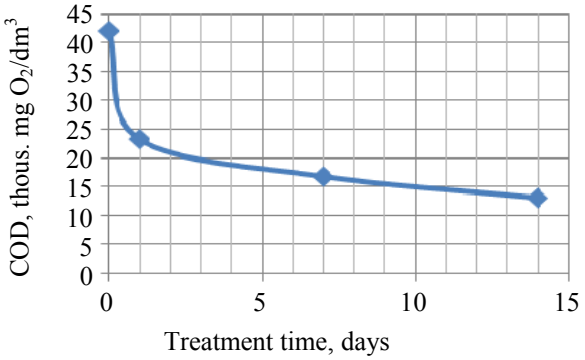

Fig. 4. The relationship between COD value and treatment time

To reduce the concentration of formaldehyde different doses of urea were added and kept for some time in acid medium (Fig. 5).

Having been kept for 4 weeks COD value decreased to 5500 mgO_2/dm^3, the concentration of free phenol decreased from 360 to 115 mg/dm^3, the formaldehyde concentration decreased from 5.00

to 0.75 g/dm^3, the methanol concentration decreased from 5.40 to 0.06 g/dm^3.

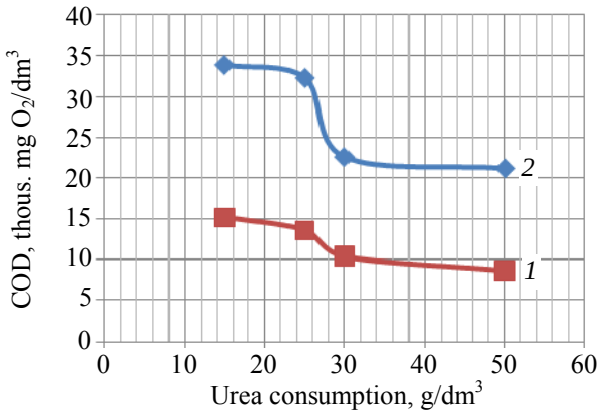

Fig. 5. The relationship between COD value and urea consumption:
1 – COD having been kept for 7 days;
2 – COD having been kept for 14 days

One of the methods of neutralizing of formaldehyde wastewater is aldol condensation of formaldehyde at elevated temperature in alkaline medium.

The treatment with calcium oxide with pH not below that 9.0 at 80 °C and above contributes a significant reduction of the formaldehyde wastewater content (by 95%) and wastewater COD (by 65%).

Pilot testing of combined methods of liquid waste treatment was carried out along with testing of the individual variants. It resulted in two options for their treatment. They differ by frequency of appending and dose of reagents.

The first example comprises the following steps: acidification, adding of urea, the addition of sorbent and neutralization.

Second case includes adding urea, acidification, addition of sorbent and neutralization.

The toxicity bioassay will be carried out to confirm the possibility of post-treatment of the neutralized liquid waste. The submission of an application for the inventions planned.

Conclusion. The methods of neutralizing of highly concentrated formaldehyde liquid waste that reduce the COD value in the first embodiment by 72% and the formaldehyde concentration by 45% were offered. The second way gives the possibility to reduce COD value by 87% and a formaldehyde concentration by 79%.

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